

## **Diamagnetism and Structure of Nitric Acid-Treated Bulk Polyethylene**

**F. Ania, F.J. Baltá Calleja and M.E. Cagiao**

Instituto de Estructura de la Materia, C.S.I.C. Serrano, 119, Madrid-6, Spain

### Summary

An alternative procedure to examine the nature of the end product of nitric-acid-treated bulk polyethylene involving the measurement of the diamagnetic susceptibility is reported. This simple non-destructive method complements previous results obtained by means of IR spectroscopy. Thus after selectively removing the surface layer of the polyethylene lamellae with nitric acid ( $t > 50h$ ) the diamagnetic susceptibility substantially decreases to values which are consistent with tilted paraffinic chains terminated by carboxyl groups including  $-NO_2$  groups in a 4:1 ratio.

### Introduction

In previous studies (PHAOVIBUL et al., 1973) the value of diamagnetic susceptibility,  $\chi_m$ , as a tool for the structure analysis of polymers was emphasized. The use of semiempirical diamagnetic increment systems (MULAY and BOUDREAU, 1976) permits, in addition, a number of structural chemical examinations and a separation of intra from intermolecular contributions to  $\chi_m$  (BALTA CALLEJA et al., 1965). In particular the susceptibility study of paraffinic monodisperse homologous series furnishes valuable data on the independent contributions from the backbone and from the chain ends to the susceptibility (BALTA-CALLEJA et al., 1976). The purpose of this work is to report the measurement of the diamagnetic specific susceptibility of the end products which result after selective oxidation of melt crystallized polyethylene treated with nitric acid. These values have been compared with experimental data on dicarboxylic acids and paraffins and those derived from increment systems to analyse the nature of the degraded molecular chains and the amount of oxidized groups introduced by the etching treatment.

### Experimental

The total defect content (branches plus unsaturations) and the defect content within crystals (CAGIAO et al., 1980) for the polyethylene samples investigated are collected in Table I. The nitric-acid degradation was performed at 60°C in open tubes during reaction times

$t > 50\text{h}$ . Further details concerning the preparation and characterization of the samples are described elsewhere (RUEDA et al., 1981). For the magnetic study the Faraday method was employed. The samples, in powder form, were tightly packed in quartz tubes (inner diameter 4 mm; height 8 mm). The tubes were placed in a double cylinder of glass in which a thermostated liquid is circulated between the constant  $B \partial B / \partial x$  pole caps of a B-M 6 Bruker electromagnet. The force acting on each sample, typically weighing  $10^{-4}\text{kg}$ , is of the order of  $10^{-5}\text{N}$  for the maximum applied magnetic field ( $\sim 1.5\text{T}$ ). For the elimination of any effects due to ferromagnetic impurities,  $\chi_m$  values were obtained from a ( $\chi_m$ ,  $1/B$ ) plot by extrapolation of  $B \rightarrow \infty$ . Each sample was measured ten times at two different field strengths in a vacuum of 1.5 Pa. At a 0.03 m gap between pole caps the  $B \partial B / \partial x$  values for 20A are respectively: 12.32 and 21.69  $\text{T}^2\text{m}^{-1}$ . In order to compare the treated polymer samples with solid dicarboxylic acids, a series of commercial (Merck) diacids were also investigated. They follow the general expression:  $(\text{COOH}-(\text{CH}_2)_n-\text{COOH})$ ;  $n = 2, 4, 5, 6, 8, 10$  and their  $\chi_m$  values (Fig. 1, full circles) have not yet been reported before. Melting points were determined with a Perkin-Elmer DSC-1B differential scanning calorimeter at a heating rate of  $8^\circ\text{C}/\text{min}$ .

### Results and Discussion

The basis of the discussion lies on the selectivity of the nitric acid reaction. It has been previously proved that with the selected degradation times the disordered material was fully digested (CAGIAO et al., 1980). Since the majority ( $> 80\%$ ) of chain defects (butyl or larger) lie admittedly on the non crystallized regions, the end product after degradation consists mainly of paraffinic chains, terminated by heavy groups with a small defect content  $\varepsilon_c < 0.01$  within the crystal. The average crystal thickness of the end product was calculated by taking into consideration the existence of two predominant lamellar thicknesses which are evidenced from the double melting temperature DSC peak in samples 1 and 2. Sample 3 shows only one single peak suggesting that only crystals with the larger thicknesses persist after the attack. The crystal thickness,  $\ell_t$ , was deduced from:  $\ell_t = 2\sigma_e T_m^\circ / (\Delta T \Delta h_c^\infty)$  where  $\sigma_e = 7.9 \times 10^{-2} \text{J m}^{-2}$ ;  $T_m^\circ = 418.5 \text{K}$ ;  $\Delta h_c^\infty = 2.8 \times 10^8 \text{J kg}^{-1}$ . This expression has been previously shown to hold in case of nitric acid treated polyethylene (ILLERS, 1968; MEINEL et al., 1970). The average crystal thickness  $\ell_t$  was finally derived from the ratio between the areas of both DSC peaks. The molecular length  $L$  has been further calculated from  $L = \ell_t / \sin \phi$  assuming a chain tilt of  $\phi \sim 34^\circ$ . Electron diffraction results (KELLER and UDAGAWA, 1971) from nitric acid isolated lamellae and electron microscopical observations on chlorosulfonated polyethylene (KANIG, 1981)

TABLE I

Defect content  $\varepsilon$ , defect content within crystals  $\varepsilon_c$ , crystal thicknesses  $\ell_t$ , molecular length  $L$ , average number  $\bar{n}$  of repeating  $-\text{CH}_2-$  units and specific susceptibility (before,  $\chi_m^b$  and after treatment,  $\chi_m^a$ ) of the samples of polyethylene.

Sample	$\varepsilon$ (%)	$\varepsilon_c$ (%)	$\ell_t$ (nm)	$\ell_t$ (nm)	$L$ (nm)	$\bar{n}$	$-\chi_m^b \times 10^{-8}$ ( $\text{m}^3 \text{kg}^{-1}$ )	$-\chi_m^a \times 10^{-8}$ ( $\text{m}^3 \text{kg}^{-1}$ )
1	1.81	0.79	12.8 9.1	10.6	12.8	101	$1.010 \pm 0.001$	$0.981 \pm 0.003$
2	3.49	0.83	8.5 6.0	7.3	8.8	69	$1.012 \pm 0.001$	$0.966 \pm 0.003$
3	6.90	0.96	7.2 -	7.2	8.7	68	$1.022 \pm 0.001$	$0.956 \pm 0.003$

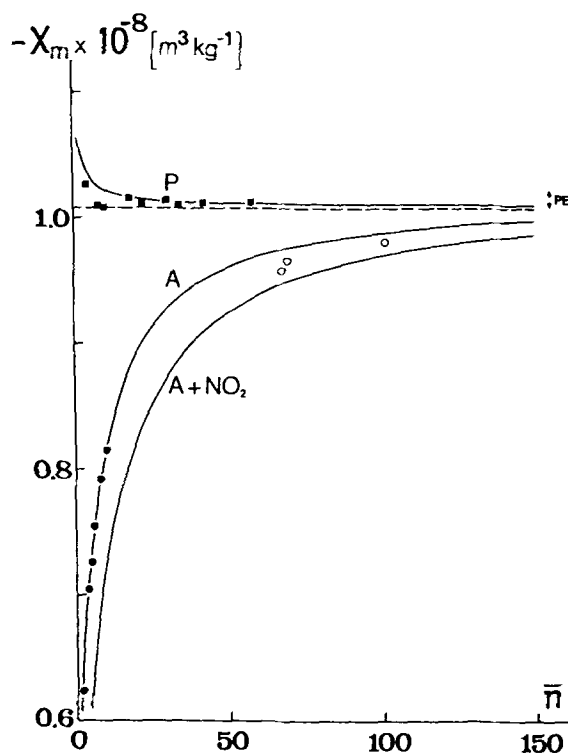


Fig. 1. Diamagnetic specific susceptibility as a function of the number  $\bar{n}$  of repeating  $-\text{CH}_2-$  units. The hyperbolic curves correspond respectively to paraffins (P), dicarboxylic acids (A) and dicarboxylic acids including a  $-\text{NO}_2$  groups per molecule ( $A + \text{NO}_2$ ). All symbols correspond to experimental values: (■) solid paraffins; (●) solid dicarboxylic acids; (○) treated PE.

confirm this tilt. Hence, the number  $\bar{n}$  of repeating  $-\text{CH}_2-$  units within the crystalline stems is  $\bar{n} = L/0.127$ , where  $0.127 \text{ nm}$  is the  $-\text{CH}_2-$  projected length. Table I gives the  $\ell_t$ ,  $\bar{\ell}_t$ ,  $L$  and  $\bar{n}$  values and the values of the specific susceptibility  $\chi_m$  of the polyethylene samples investigated before and after nitric acid treatment. The  $\chi_m$  substantial decrease after treatment is evident. The  $\chi_m$  values for the treated samples are represented by open circles in Fig. 1. The hyperbolic curves correspond respectively to the specific diamagnetic susceptibility values of a series of paraffins (P) in the solid state (BALTA-CALLEJA et al., 1976), dicarboxylic acids (A) and dicarboxylic acids including a  $-\text{NO}_2$  group per molecule (A +  $\text{NO}_2$ ). These curves follow the general expression:

$$\chi_m = \frac{n \chi_p + b_p}{n M_1 + M_2} \quad \text{where} \quad \chi_p \approx 1.42 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$$

represents the contribution to the molecular diamagnetism of the  $-\text{CH}_2-$  group and  $b_p$  is the contribution associated to the end groups ( $b_p = -3.27 \times 10^{-10}$ ,  $-4.54 \times 10^{-10}$  and  $-5.54 \times 10^{-10} \text{ m}^3 \text{ mol}^{-1}$  for P, A and A +  $\text{NO}_2$  respectively).  $M_1$  and  $M_2$  are the molecular masses for a  $-\text{CH}_2-$  group and the corresponding end groups respectively. The P and A curves were calculated from the experimental values of solid paraffins (full squares) and solid dicarboxylic acids (full circles). The curve A +  $\text{NO}_2$  has been calculated from the susceptibility increments assuming that each molecule is a dicarboxylic acid including one  $\text{NO}_2$  group. It is noteworthy that the susceptibility values obtained from any increment system are frequently higher than the experimental values in the solid state. This is because such increment systems do not include intermolecular interactions. However, in the case of dicarboxylic acids, curve A practically coincides with the one calculated from the increments' method. As  $n \rightarrow \infty$ ,  $\chi_m \approx \chi_p/M_1$ , i.e. the hyperbolae asymptotically approach the  $\chi_m$  value of an infinite paraffinic chain (straight dotted line in Fig. 1). It is seen that the experimental values of treated polyethylene (open circles) are lying below curve A and well below curve P. This result confirms, that for long treatment times ( $> 50 \text{ h}$ ) the paraffinic character of the molecular chains is lost and the crystals consist mainly of chains terminated by  $\text{COOH}$  groups. The presence of  $\sim 1\%$  chain defects per  $10^2 \text{ CH}_2$  within the crystals does not seem to affect the  $\chi_m$  value. This value is, however, somewhat elevated in case of chain systems containing backbone defects (ANIA et al., 1979). In our case the concentration of defects is probably too low to be detected by magnetic susceptibility. Otherwise this  $\chi_m$  value would fit with the view of stems containing branches within the crystals as almost perfect space filling

point defects. The observed depression of magnetic susceptibility from curve A (dicarboxylic acids) could be explained by the introduction of additional groups which contribute to a lowering of the susceptibility value. IR data (RUEDA et al., 1981) suggest the nitro group as the most probable candidate. The experimental susceptibility data lie between curves A and A+NO<sub>2</sub>. Hence, it can be concluded that one nitro group every two molecules i.e. a ratio of nitro to carboxyl groups of 1:4, occurs. In summary, the present study offers new aspects of the degradation mechanism of PE with FNA highlighting the diamagnetic susceptibility method as capable to detect with certain detail the drastic change from the initial two-phase PE structure into the final paraffinic system and to furnish a separate confirmation on the nature of oxidized groups.

#### References

- ANIA, F., BALTA-CALLEJA, F.J. and DE ABAJO, J.  
J. Macromol. Sci., B16, 377 (1979)
- BALTA-CALLEJA, F.J., HOSEMAN, R. and WILKE, W.  
Trans. Faraday Soc., 61, 1912 (1965)
- BALTA-CALLEJA, F.J., BERLING, K.D., CACKOVIC, H., HOSEMAN, R.  
and LOBODA-CACKOVIC, J., J. Macromol. Sci., B12, 383 (1976)
- CAGIAO, M.E., RUEDA, D.R. and BALTA-CALLEJA, F.J.  
Polymer Bulletin, 3, 305 (1980)
- ILLERS, K.H.  
Makromol. Chem., 118, 88 (1968)
- KANIG, G.  
30. Meeting Kolloid-Gesells. 9 Oct. Ulm (1981)
- KELLER, A. and UDAGAWA, Y.  
J. Polym. Sci., Part A-2, 9, 1793 (1971)
- MEINEL, G., MOROSOFF, N. and PETERLIN, A.  
J. Polym. Sci., Part A-2, 8, 1723 (1970)
- MULAY, L.N. and BOUDREAUX, E.A.  
(Editors) "Theory and Applications of Molecular  
Diamagnetism", Wiley, New York (1976)
- PHAOVIBUL, O. LOBODA-CACKOVIC, J. HOSEMAN, R. and  
BALTA-CALLEJA, F.J., J. Polymer Sci. Polym. Physics,  
11, 2273 (1973)
- RUEDA, D.R., CAGIAO, M.E. and BALTA-CALLEJA, F.J.  
Makromol. Chem., 182, 2705 (1981)

#### Acknowledgment

Grateful acknowledgment is due to the CAICYT for the support of this work and to the Alexander von Humboldt Stiftung for the generous supply of the Bruker Susceptibility System.

*Received May 4, accepted May 7, 1982*